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Detailed Description of the Invention

The present invention relates to a method of producing higher alcohol-based anionic surface active agents. More particularly, the present invention relates to a method for the production of novel surface active agents comprising higher alcohol sulphate ester salts by subjecting vinylidene type olefin, obtained by the dimerization of  $\alpha$ -olefin, to an oxo reaction and to a hydrogenation reaction, so as to produce a so-called oxo alcohol, after which this is sulphated.

The chief anionic surface active agents used or known hitherto as surfactants and, in particular, as detergent materials, are alkylbenzenesulphonates which employ propylene tetramer as the raw material component, and higher alcohol sulphate ester salts formed from either naturally-occurring straight chain alcohols or the oxo alcohols obtained by subjecting a straight chain  $\alpha$ -olefin to the oxo reaction process, etc.

However, while surfactants in which an aforesaid alkylbenzenesulphonate is the chief component are outstanding in their surface activity and detergency, their biodegradability is extremely poor, so the waste liquids following the use of such surface active agents do not break down when discharged into rivers, etc, and therefore pollute the rivers. Consequently, for reasons such as a fear that they will become mixed into drinking water, their use is gradually being cut back.

Again, while surface active agents comprising the aforesaid higher alcohol sulphate ester salts, which were developed as surface active agents with good biodegradability, are indeed excellent in terms of their biodegradability and so do not pollute rivers, their low temperature surface activity and detergency are not

altogether satisfactory since they have low solubility at low temperatures.

Now, as the raw material olefin for the higher alcohol sulphate ester based surfactants, as well as the aforesaid straight chain  $\alpha$ -olefins there can also be considered the use of various types of branched olefins. For example, there is the dodecene obtained by the tetramerization of propylene by means of an acid catalyst, or the dodecene obtained by first subjecting propylene to dimerization using a transition metal oxide catalyst such as nickel oxide or chromium oxide, and then subjecting the hexene-2, hexene-3, etc, thus obtained, to further dimerization using a transition metal oxide catalyst.

However, the structure of the raw material olefin obtained by this method is not uniform, and it comprises many types of isomers where the position of branching or the number of carbons in the branch chain differs, and when the oxo reaction is then carried out using this mixture, even more isomers are produced. Consequently, a detergent obtained via the oxo alcohol from such a reaction product is itself an extremely complex mixture containing considerable amounts of material with outstanding biodegradability and poor detergency, outstanding detergency and poor biodegradability, and both poor biodegradability and poor detergency, etc. Thus, it is not possible to produce, selectively, material with the desired detergency and biodegradability.

The present inventors have carried out extensive research into olefin oligomerization methods and into surface active agents utilizing the branched olefins obtained by such methods, with the aim in particular of establishing an industrially valuable method for the

production of surfactants with outstanding detergency at low temperature and which also have good biodegradability. As a result, they have obtained the following novel findings.

Specifically they have found that if an  $\alpha$ -olefin is dimerized using an alkylaluminium compound as the catalyst and the vinylidene type olefin thus obtained then used as the raw material olefin in the oxo reaction, after which hydrogenation is performed, the structure of the oxo alcohol obtained invariably has uniform branching due to the characteristics of the dimerization and oxo reactions, and when the higher alcohol sulphate ester salt obtained by subjecting this oxo alcohol to sulphation and neutralization is used as a surface active agent, it exhibits high water solubility at low temperatures, so, consequently, its low temperature surface activity and detergency are particularly outstanding and, moreover, it has excellent biodegradability. When compared to conventional higher alcohol-based surface active agents, it is excellent as a low temperature surface active agent and detergent, and thus it is fully effective as a low temperature detergent, in particular as a liquid detergent.

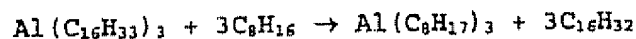
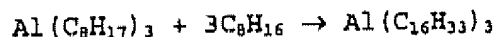
The present invention has been made based on these findings, and its characteristic feature is that a  $C_8$  to  $C_{20}$  vinylidene type olefin, or mixture thereof, obtained by the dimerization of a  $C_4$  to  $C_{10}$   $\alpha$ -olefin, or mixture thereof, using an alkylaluminium catalyst, is subjected to reaction with carbon monoxide and hydrogen in the presence of an oxo reaction catalyst, and then the product subjected to hydrogenation, after which the  $C_8$  to  $C_{21}$  higher alcohol or higher alcohol mixture thereby obtained is sulphated, and then neutralized, to produce

a surfactant comprising a higher alcohol sulphate ester salt.

Next, explaining the present invention in further detail, the  $C_4$  to  $C_{10}$   $\alpha$ -olefin used in the dimerization in the method of the present invention can be obtained by any means, and may be for example the lower  $\alpha$ -olefin produced by an ethylene oligomerization reaction or the comparatively low  $\alpha$ -olefin obtained by the decomposition of paraffin wax.

In the dimerization of these  $\alpha$ -olefins it is necessary to use an alkylaluminium compound as the catalyst at the time of said reaction and, normally, there is used a trialkylaluminium such as triethylaluminium, a dialkylaluminium monohydride such as diethylaluminium monohydride, a monoalkylaluminium dihydride such as monoethylaluminium dihydride, a dialkylaluminium monohalide such as diethylaluminium monochloride, or a monoalkylaluminium dihalide such as monoethylaluminium dichloride. With regard to the length of the carbon chain in the alkyl group, since the catalyst is an intermediate in the dimerization reaction as shown by the reaction scheme given below, it has an influence on the length of the carbon chain of the vinylidene type olefin produced. Hence, it is preferred that there be used an alkyl aluminium compound having an alkyl group (or groups) of appropriate chain length corresponding to the carbon chain length of the desired vinylidene olefin. For example, there is used an alkylaluminium compound with a straight chain alkyl group (or groups) which has the same number of carbons as the raw material  $\alpha$ -olefin, or one having an alkyl group (or groups) which can readily be replaced by such an alkyl group (for example the isobutyl group).

For example, in the case where octene-1 is subjected to a dimerization reaction using trioctylaluminium as the catalyst, the reaction proceeds as follows to produce the dimer of octene-1.



The amount of such catalyst used is normally 0.005 to 10 mol, and preferably 0.02 to 0.2 mol, per mol of the  $\alpha$ -olefin raw material. The dimerization reaction is carried out by mixing together the  $\alpha$ -olefin raw material and the alkylaluminium in these proportions, with the reaction conditions normally comprising a reaction temperature of 100-250°C, preferably 140-200°C, and a reaction pressure in the range from normal pressure to 100 atmospheres.

The reaction product obtained by dimerization under these conditions is normally an  $\alpha$ -olefin in which at least 90% branches at the 2-position, i.e. a vinylidene type olefin, and this vinylidene type olefin is then subjected to an oxo reaction and a hydrogenation reaction to produce the alcohol.

In the oxo reaction, reaction is conducted with the introduction of carbon monoxide and hydrogen. The amounts thereof introduced can have various proportions in the range  $\text{H}_2 : \text{CO} = 1 : 3$  to  $3 : 1$  but normally it is preferred that they are mixed in  $1 : 1$  proportions. Once again, it is necessary that this oxo reaction be carried out using a catalyst, and a rhodium catalyst or cobalt catalyst is generally employed.

Examples of the rhodium catalyst are rhodium sulphate, rhodium oxide, rhodium chloride, ammonium chlororhodate and other such inorganic salts, rhodium formate and other such organic salts, triphenylphosphine rhodium, rhodium acetylacetonate and other such organometallic complex compounds, and also rhodium metal and rhodium carbonyl.

The amount of the rhodium catalyst used is normally about 0.1 to 500 mg (as metal rhodium) per litre of oxo reaction liquid (the raw material olefin plus the reaction medium).

Furthermore, as the cobalt catalyst there may be used, for example, cobalt laurate, cobalt naphthenate or other such organic salt, or cobalt carbonyl. The amount of cobalt catalyst employed is normally about 0.5 to 10 g (as cobalt metal) per litre of the oxo reaction liquid.

Again, it is preferred in terms of promoting the reaction that in said reaction there be present a reaction medium, examples of which are aromatic hydrocarbons such as benzene and toluene, aliphatic hydrocarbons such as hexane and octane, alcohols such as methanol, ethanol and cyclohexanol, and ketones.

In the presence of such catalyst and reaction medium, the carbon monoxide and hydrogen are introduced mixed in the specified proportions, and reaction is carried out normally at a reaction temperature of 30 to 300°C, and preferably 60 to 200°C, at a reaction pressure of at least 20 atmospheres, preferably 100 to 300 atmospheres. Following the end of the reaction, the oxo reaction liquid obtained, which chiefly comprises aldehyde, is either subjected to hydrogenation as it is or after

removal of the reaction catalyst, and conversion thereby performed to the alcohol.

This hydrogenation reaction is either carried out for example while still containing the rhodium or cobalt catalyst following the oxo reaction, within the temperature range 100 to 300°C, and at a higher temperature than that required for the oxo reaction, at a concentration of hydrogen higher than that in the oxo reaction gas, or alternatively it is carried out after removing the oxo reaction catalyst from the oxo reaction product liquid, with the addition of a hydrogenation catalyst optionally supported on diatomaceous earth, for example a nickel catalyst or copper-chromite catalyst, and hydrogenation carried out at normal pressure or under applied pressure following the introduction of the hydrogen. After the reaction, the alcohol is recovered by distillation from the reaction product liquid. The oxo alcohol obtained in this way is primarily a C<sub>9</sub> to C<sub>11</sub> primary alcohol which branches at the 3-position, and this is then sulphated. As the sulphating agent employed in this sulphation, there is used concentrated sulphuric acid, fuming sulphuric acid, chlorosulphonic acid, sulphuric anhydride (SO<sub>3</sub>)-air, sulphuric anhydride-nitrogen, sulphuric anhydride-liquid sulphurous acid, or the like.

The ideal amount of sulphating agent employed will differ with the type of sulphating agent used. For example, in the case where concentrated sulphuric acid is used, from 1.5 to 2.0 mol per mol of the starting material alcohol is suitable. Furthermore, in the case where chlorosulphonic acid is used, about 1.0 to 1.1 mol per mol of the starting material alcohol is suitable. Normally, there should be used from about 0.9 to 2.0 mol per mol of the starting material alcohol.



The sulphation is carried out using an aforesaid sulphating agent under conditions normally comprising a temperature of no more than 60°C, and preferably around 30°C, at normal pressure.

Again, where required there may be employed an inert solvent such as chloroform, carbon tetrachloride or the like.

Following the end of the sulphation reaction, neutralization is carried out by the addition of a suitable base to the sulphated product, while preventing any rise in temperature as far as possible. That is to say, if the liquid temperature is allowed to rise due to the neutralization reaction, the higher alcohol sulphate ester salt produced becomes discoloured and its value as a product is lowered. Hence, at the time of neutralization it is preferred that said neutralization be carried out with the addition of a suitable diluent, for example water-containing isopropyl alcohol or the like.

Examples of the base material used in the neutralization are metal hydroxides such as sodium hydroxide, potassium hydroxide, calcium hydroxide and magnesium hydroxide, organic amines such as diethanolamine and triethanolamine, or ammonia. However, in general sodium hydroxide is widely employed.

The amount of the base material used for the neutralization will be about the stoichiometric quantity. For example, in the case where 1.5 mol of concentrated sulphuric acid has been employed per mol of the starting material alcohol, about 2 mol of sodium hydroxide is required. The neutralized reaction product can then be purified by a process such as dissolving in

a suitable solvent and eliminating the inorganic salt, or it can also be used as a surface active agent as it is, still containing the by-product sodium sulphate.

From the higher alcohol sulphate ester salt obtained in this way, the desired surface active agent can be obtained by compounding this surface active agent with, as and where required, other suitable surface active agents, or builders or bulking agents such as sodium sulphate, phosphates, carboxymethylcellulose, fluorescent whitening agents and the like.

As explained above, when producing a surface active agent in accordance with the method of the present invention, an oxo alcohol of uniform chemical structure is obtained using a  $C_4$  to  $C_{10}$ , preferably a  $C_6$  to  $C_{10}$ , lower  $\alpha$ -olefin as the starting material, and this oxo alcohol is then converted to the sulphate ester salt, to provide a surface active agent with extremely outstanding low temperature detergency and, furthermore, with sufficient biodegradability.

Next, detailed embodiments of the method of the present invention are explained by means of examples but, providing that the essence of the invention is retained, there is no restriction to the examples given.

#### Example 1

##### (a) Dimerization of the $\alpha$ -olefin

15 mol of hexene-1 and 1 mol of trihexylaluminium  $[Al(C_6H_{13})_3]$  were mixed together and the mixture introduced into an autoclave. Reaction was carried out for about 7 hours at normal pressure with the reaction temperature maintained at  $150^\circ C$  while stirring, as a result of which there was obtained a reaction product

containing 4.9 mol of dimer olefin, at a percentage conversion of 65%.

Next, this reaction product was subjected to distillation under reduced pressure and the unreacted hexene-1 and dimer olefin distilled off and recovered. Moreover, the trihexylaluminium was obtained as the distillation residue. The distillate comprising unreacted hexene-1 and dimer olefin was further distilled to mutually separate these components. The unreacted hexene-1 and the trihexylaluminium were recycled to the dimerization reaction.

94% of the dimer olefin obtained was vinylidene type olefin, while the rest was of the internal olefin type. The dimer olefin was then supplied to the following oxo reaction for conversion to the alcohol.

#### (b) Production of the alcohol

40 ml of the dimer olefin obtained by the method in (a) above, plus 0.2 ml of an aqueous rhodium nitrate solution of concentration 2 g/litre (as metal rhodium) (which corresponded to an amount of added catalyst rhodium of 10 mg per litre of the oxo reaction liquid) were introduced into an electromagnetically-stirred autoclave of internal capacity 200 ml and, after flushing out the atmosphere inside the autoclave with carbon monoxide, there was introduced carbon monoxide at room temperature up to a pressure of 90 atmospheres, and then the temperature raised to 120°C. The carbon monoxide pressure at this time was 120 atmospheres. After maintaining for 10 minutes at this temperature, hydrogen was introduced and when the total pressure was 240 atmospheres, reaction commenced. Over about 120 minutes, 58 atmospheres of gas was absorbed, by which time the reaction had largely come to a halt.

After the end of the reaction the autoclave was cooled, and the reaction product introduced into a shaking-type autoclave of internal capacity 200 ml, along with 10 g of a diatomaceous earth-supported nickel catalyst which had been reduced beforehand with hydrogen. 100 atmospheres of hydrogen was introduced at normal temperature, then the temperature raised to 160°C and reaction carried out while shaking for 5 hours. Following the reaction, the catalyst was filtered off from the reaction product, and then tridecyl alcohol obtained by distillation under reduced pressure. Now, the overall yield from the oxo reaction to the hydrogenation reaction was 84%.

(c) Production of the sulphate ester salt

1 mol of the tridecyl alcohol obtained by the method in (b) above was introduced into a four-necked flask equipped with a stirrer, thermometer, reflux condenser and dropping funnel and, while maintaining the reaction temperature at about 30°C, 1.1 mol of chlorosulphonic acid was added dropwise from the dropping funnel and the sulphation reaction carried out.

Following the completion of the dropwise addition of the chlorosulphonic acid, the reaction liquid was diluted with 90% isopropyl alcohol and then neutralization carried out by the addition of a calculated quantity of aqueous sodium hydroxide solution. Following the neutralization, the reaction liquid was heated to 80°C and the by-product inorganic salt filtered off, after which the isopropyl alcohol was distilled off. The reaction product was then dissolved in methanol and inorganic salt again filtered off, after which the methanol was distilled off.

In this way tridecyl alcohol sulphate ester sodium salt was obtained at a yield of 98%.

### Example 2

#### (a) Dimerization of the $\alpha$ -olefin

10 mol quantities of hexene-1, octene-1 and decene-1 respectively, plus 1 mol of triisobutylaluminium, were mixed together and the mixture introduced into an autoclave. Reaction was carried out for about 6 hours at normal pressure while stirring with the reaction temperature maintained at 160°C, after which distillation was performed under reduced pressure. 0.9 mol, 1.8 mol, 2.7 mol, 1.8 mol and 0.9 mol of dimer olefins with 12, 14, 16, 18 and 20 carbons respectively were obtained. 94% of the dimer olefin was vinylidene type olefin and 6% was of the internal olefin type. The dimer olefin was supplied to the subsequent oxo reaction for conversion to the alcohol.

#### (b) Production of the alcohol

100 ml of the dimer olefin mixture obtained by the method in (a) above, plus 0.5 ml of an aqueous rhodium acetate solution of concentration 2 g/litre (as metal rhodium) (which corresponded to an amount of added catalyst rhodium of 10 mg per litre of the oxo reaction liquid), were introduced into an electromagnetically-stirred autoclave of internal capacity 500 ml and, after flushing out the atmosphere inside the autoclave with carbon monoxide, there was introduced carbon monoxide at room temperature up to a pressure of 93 atmospheres, and then the temperature raised to 120°C. The carbon monoxide pressure at this time was 120 atmospheres. After maintaining for 10 minutes at this temperature,

hydrogen was introduced and when the total pressure was 200 atmospheres, reaction commenced. Over about 180 minutes, 53 atmospheres of gas was absorbed, by which time the reaction had largely come to a halt.

Using 16 g of the same hydrogenation catalyst as in Example 1, this oxo reaction product was hydrogenated in the same way as in Example 1, then reduced pressure distillation carried out at 100-185°C/5 mmHg. The C<sub>13</sub> to C<sub>21</sub> alcohol fraction was obtained at an overall yield of 95% for the oxo reaction and the hydrogenation reaction. The alcohol content of this fraction was 92%.

(c) Production of the sulphate ester salt

The C<sub>13</sub> to C<sub>21</sub> alcohol obtained by the method in (b) above was subjected to sulphation in exactly the same way as in Example 1 and then neutralized. Sulphate ester sodium salt was obtained at a yield of 96%.

Example 3

Except that the dimerization of octene-1 was carried out using trioctylaluminium, (a) the dimerization of the  $\alpha$ -olefin, (b) the production of the alcohol and (c) the production of the sulphate ester salt were respectively carried out in the same way as in Example 1, and the C<sub>17</sub> alcohol sulphate ester sodium salt obtained.

Example 4

Except that (a) the dimerization of the  $\alpha$ -olefin was carried out using decene-1 and tridecylaluminium, and then (b) the production of the alcohol was carried out as described below, the C<sub>21</sub> alcohol sulphate ester sodium salt was obtained in exactly the same way as in Example 1.

(b) Production of the alcohol

100 ml of the decene-1 dimer olefin obtained by reaction in the same way as in Example 1 plus 0.5 ml of an aqueous rhodium acetate solution of concentration 2 g/litre (as metal rhodium) (which corresponded to an amount of added catalyst rhodium of 10 mg per litre of the oxo reaction liquid) were introduced into an electromagnetically-stirred autoclave of internal capacity 500 ml and, after flushing out the atmosphere inside the autoclave with carbon monoxide, there was introduced carbon monoxide at room temperature up to a pressure of 93 atmospheres, and then the temperature raised to 110°C. The carbon monoxide pressure at this time was 120 atmospheres. After maintaining for 10 minutes at this temperature, hydrogen was introduced and when the total pressure was 200 atmospheres, reaction commenced. Over about 100 minutes, 43 atmospheres of gas was absorbed, by which time the reaction had largely come to a halt.

This oxo reaction product was subjected to hydrogenation in the same way as in Example 1 using 16 g of the same hydrogenation catalyst as in Example 1, after which distillation was performed and C<sub>21</sub> alcohol obtained at an overall yield of 82%.

Next, results are given for tests carried out on the various alcohol sulphate ester salts obtained by the methods in the above examples, to determine their detergent capacity and other interfacial properties, and also their biodegradability.

Test Example 1:

Test of surface active agent properties (other than detergency)

The surface active properties of the alcohol sulphate ester salts obtained in Examples 1 to 4, that is to say the alcohol sulphate ester sodium salts obtained from the vinylidene type olefin oxo alcohols, were measured by means of the following methods. The results are shown in the tables below. For comparison, there are also shown in the tables the measurement results for the surface active properties of alcohol sulphate ester sodium salts obtained using the oxo alcohols derived from straight chain  $\alpha$ -olefins with the same number of carbon atoms as the aforesaid vinylidene olefins, as starting materials.

(1) Surface tension

The surface tension was measured for aqueous solutions of sample concentration 0.05%, 0.1% and 0.2% at 10°C and 40°C by means of the method of ASTM D-1331-56 described in the "Yushi Kagaku Benran" (Oil & Fats Chemistry Handbook) page 489, the so-called DuNouy method.

(2) Foaming strength

Using the so-called Ross-Miles method described in JIS K-3362, 1955 (Test Methods for Synthetic Detergents), the height of the foam was measured directly after the end of the pouring down of the test solution, using aqueous solutions of sample concentration 0.05%, 0.1% and 0.2% at temperatures of 10°C and 40°C.

(3) Permeation strength

Based on the method described in "Yukagaku" (J. Japan Oil Chemists' Society) Vol. 11, No.4, pp183-190 (1962),



a 1 inch diameter felt disc was placed on a disc support made of stainless steel wire horizontally provided at the bottom end of an inverted Kuuchi glass funnel and this then immersed in 50 ml of an aqueous solution of the sample of concentration 0.05%, 0.1% or 0.2%, at 10°C or 40°C, and forcibly held 1/2 inch below the liquid surface. The time was measured for sinking to occur after the disc was immersed in the sample solution.

Table 1

(a) Measurement Results at 10°C

Sample	Detergency (dyne/cm)			Foaming Strength (cm)			Permeation (secs)		
	0.05%	0.1%	0.2%	0.05%	0.1%	0.2%	0.05%	0.1%	0.2%
$\alpha$ -C <sub>13</sub>	41.3	37.2	32.8	11.5	14.5	16.0	1662	287	45.9
VT-C <sub>13</sub>	33.5	32.4	31.9	14.0	19.0	20.0	1308	200	26.2
$\alpha$ -C <sub>17</sub>	38.4	37.7	37.2	7.5	8.0	6.5	876	359	108
VT-C <sub>17</sub>	29.7	28.6	27.8	16.5	17.5	18.5	114	12.7	5.6
$\alpha$ -C <sub>21</sub>	45.5	43.9	43.2	1.5	1.5	1.5	-	-	-
VT-C <sub>21</sub>	31.0	29.6	28.5	8.0	8.5	10.0	320	105	83.0
VT-C <sub>12-21</sub>	31.6	30.9	29.9	17.0	17.5	18.0	235	54.3	20.1

In the sample column in the table above,  $\alpha$ -C<sub>13</sub> denotes the C<sub>13</sub> oxo alcohol sulphate ester sodium salt obtained via a straight chain  $\alpha$ -olefin oxo reaction, and VT-C<sub>13</sub> denotes the C<sub>13</sub> oxo alcohol sulphate ester sodium salt derived from the vinylidene type olefin produced in accordance with the present invention. The same is true for the other sample codes given, except that the number of carbons is different.

Table 2

(a) Measurement Results at 40°C

Sample	Detergency (dyne/cm)			Foaming Strength (cm)			Permeation (secs)		
	0.05%	0.1%	0.2%	0.05%	0.1%	0.2%	0.05%	0.1%	0.2%
$\alpha$ -C <sub>13</sub>	43.6	37.0	36.4	17.0	19.5	22.0	670	16.0	8.9
VT-C <sub>13</sub>	44.3	39.9	32.9	11.0	15.0	19.0	33.6	221	4.4
$\alpha$ -C <sub>17</sub>	37.0	38.0	37.3	23.0	24.0	24.0	240	64.0	11.5
VT-C <sub>17</sub>	32.0	31.5	30.9	20.5	21.5	21.5	28.2	3.7	2.2
$\alpha$ -C <sub>21</sub>	44.8	43.9	44.1	1.5	1.5	1.5	-	-	3000

VT-C <sub>11</sub>	31.0	29.8	29.1	13.0	14.0	14.0	51.8	25.5	21.8
VT-C <sub>11-11</sub>	31.2	30.4	29.7	18.5	19.0	19.5	29.5	10.6	6.7

In the sample column, the codes have the same meanings as above.

#### Test Example 2:

Based on the detergency test method tentatively proposed by the Japan Oil Chemists' Society Detergency Test Committee (see "Yushi Kagaku Benran" (Oil & Fats Chemistry Handbook; Ed. by the Japan Oil Chemists' Society) pp 654-656, published by Maruzen 1958), there was used as test-pieces artificially soiled cotton cloth (as specified by the Detergency Test Committee), and washing was carried out at 15°C or 40°C in a Launder Tester (model LT-20, manufactured by the Shimadzu Corporation) using 0.1% aqueous solutions of the samples tested in Test Example 1 above. The detergent efficiency was calculated from the test piece reflectance using the following formula.

$$\text{detergent efficiency} = \frac{\text{reflectance of washed material} - \text{reflectance of soiled material}}{\text{reflectance of original material} - \text{reflectance of soiled material}} \times 100$$

Sample	Cotton Detergency (D%)	
	15°C	40°C
α-C <sub>13</sub>	25	30
VT-C <sub>13</sub>	12	20
α-C <sub>17</sub>	38	48
VT-C <sub>17</sub>	58	67
α-C <sub>21</sub>	13	30
VT-C <sub>21</sub>	25	45
VT-C <sub>13-21</sub>	32	46

The codes used in the sample column have the same meanings as above.

From the above tables, it can be seen that, except in the case where a comparatively low carbon number material is used on its own, the alcohol sulphate ester salts obtained by the method of the present invention show quite outstanding detergency when compared to alcohol sulphate ester salts derived from conventional straight-chain  $\alpha$ -olefins via the oxo reaction.

#### Test Example 3:

##### Biodegradability test

A comparison was carried out by the following test method of the levels of biodegradation of a surface active agent produced by the method of the present invention and a surface active agent with a long-chain alkyl group, namely sodium p-(n-dodecyl)benzene sulphonate, which is employed in the US and Europe as a 'softer' detergent with good biodegradability, with these surfactants being degraded by micro-organisms contained in activated sludge.

Firstly, 300 ml of an aqueous solution of the sample of concentration 20 ppm was placed in a 500 ml conical flask, and 3 ml of activated sludge (taken from a sewage treatment plant aeration tank) added and the mixture left at room temperature (5 to 15°C). Culturing was carried out while constantly introducing air into the sample solution.

From the test liquid subjected to continuous culturing in this way, portions were taken at 24 hours intervals and the amount of test sample remaining in the test liquid determined. Specifically, a methylene blue colorimetric determination was performed by the Longwell-Maniece method described in the Analyst Vol.80

(1955) page 167, and from the result the residual amount of surface active agent was calculated. The measurement results for each sample are shown in the following table.

Type of Surfactant	Residual Amount of Sample (%) after				
	1 day	2 days	3 days	4 days	5 days
Sodium p-(n-dodecyl)benzene-sulphonate	97.8	98.0	87.8	70.6	48.7
C <sub>11</sub> alcohol sulphate ester Na salt obtained by the method of the present invention (Example 3)	92.1	72.0	55.0	40.0	25.6

It is clear from the above table that the alcohol sulphate ester salt obtained by the method of the present invention is even softer<sup>1</sup> than a surface active agent generally regarded as being of the softer type, and with this level of biodegradability it is fully employable in the form of detergents or other type of surface active agents.

#### Scope of Claim

A method of producing higher alcohol sulphate ester salts which is characterized in that a C<sub>4</sub> to C<sub>10</sub>  $\alpha$ -olefin or mixture thereof is dimerized using an alkylaluminium compound as catalyst, and the C<sub>8</sub> to C<sub>20</sub> vinylidene type olefin or mixture thereof obtained is reacted with carbon monoxide and hydrogen in the presence of an oxo reaction catalyst, and then the product hydrogenated, after which the C<sub>9</sub> to C<sub>21</sub> higher alcohol or mixture thereof obtained is sulphated and neutralized.

Translator's Note

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<sup>1</sup> Presumably the term 'softer' here means the ease of biodegradation.